The Dynamics of Supercooled Silica: Acoustic modes and Boson peak

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Using molecular dynamics computer simulations we investigate the dynamics of supercooled silica in the frequency range 0.5-20 THz and the wave-vector range 0.13-1.1Å^{-1}. We find that for small wave-vectors the dispersion relations are in very good agreement with the ones found in experiments and that the frequency at which the boson-peak is observed shows a maximum at around 0.39Å^{-1}.

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I. INTRODUCTION

In the last few years a significant effort was undertaken to understand the nature of the so-called boson-peak, a prominent dynamical feature at around 1 THz which is observed in strong glassformers [1–4]. Various theoretical approaches have been proposed to explain this peak, such as localized vibrational modes or scattering of acoustic modes, but so far no clear picture has emerged yet. Recently also computer simulations have been used in order to gain insight into the mechanism that gives rise to this peak, but due to the high cooling rates with which the samples were prepared (on the order of 10^{12}K/s) and small system sizes (20-40Å) the results of these investigations were not able to give a final answer either [2,4]. In the present work we present the results of a large scale computer simulation of supercooled silica. At the temperature investigated we are still able to fully equilibrate the sample, thus avoiding the problem of the high cooling rates, and by using a large system we can minimize the possibility of finite size effects [5]. Thus, by making a large computational effort, we are able to study the dynamics of this strong glassformer in a frequency and wave-vector range which is not accessible to real experiments and can therefore investigate the properties of the boson-peak in greater detail than was possible so far.

II. DETAILS OF THE SIMULATIONS

The silica model we use for our simulation is the one proposed by van Beest *et al.* [6] and has been shown to give a good description of the static properties of silica glass [7] as well as the dynamical properties of the supercooled melt, such as the activation energy of the diffusion constant [8]. In this model the potential between ions i and j is given by

$$\phi(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij}e^{-B_{ij}r_{ij}} - \frac{C_{ij}}{r_{ij}^6} \quad . \tag{1}$$

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The values of the parameters q_i, A_{ij}, B_{ij} and C_{ij} can be found in the original publication [6]. The non-Coulombic part of the potential was truncated and shifted at 5.5Å. The simulations were done at constant volume and the density of the system was fixed to 2.3 g/cm^3. The system size was 8016 ions, giving a size of the box of $(48.37\text{Å})^3$, and the equations of motion were integrated over $4 \cdot 10^6$ times steps of 1.6fs, thus over a time span of 6.4ns. This time is sufficiently long to fully equilibrate the system at 2900K, the temperature considered in this study [8]. More details on the simulations can be found in Ref. [9].

III. RESULTS

In the present work we study the dynamics of the system by means of $J_L(q,\nu)$ and $J_T(q,\nu)$, the longitudinal and transverse current-current correlation functions for wave-vector q at frequency ν [10]. These are defined as the longitudinal and transverse part of the current-current correlation function, i.e.

$$J_\alpha(q,\nu) = N^{-1} \int_{-\infty}^{\infty} dt \exp(i2\pi\nu t) \sum_{kl} \langle \mathbf{u}_k(t) \cdot \mathbf{u}_l(0) \exp(i\mathbf{q} \cdot [\mathbf{r}_k(t) - \mathbf{r}_l(0)]) \rangle \quad , \qquad (2)$$

where $\mathbf{u}_k(t)$ is equal to $\mathbf{q} \cdot \dot{\mathbf{r}}_k(t)/q$ for $\alpha = L$ and equal to $\mathbf{q} \times \dot{\mathbf{r}}_k(t)/q$ for $\alpha = T$. Note that $J_L(q,\nu)$ is also equal to $\nu^2 S(q,\nu)/q^2$, where $S(q,\nu)$ is the dynamical structure factor as measured in scattering experiments. In the following we will focus on the silicon-silicon correlation only, but we have found that the oxygen-oxygen correlation function behave very similarly.

In Fig. 1 we show the frequency dependence of $J_L(q,\nu)$ for wave-vectors between 0.13Å^{-1}, the smallest wave-vector compatible with our box, and 0.8Å^{-1}, a wave-vector which is still significantly smaller than the location of the first sharp diffraction peak in $S(q)$, which is around 1.6Å^{-1}. From the figure we recognize that this correlation function has a peak at a frequency $\nu_L(q)$ which increases with increasing q and which correspond to the longitudinal acoustic modes. A similar picture is obtained for $J_T(q,\nu)$ [9]. The fact that also this correlation function shows an acoustic mode shows that even at this relatively high temperatures the system is able to sustain transverse acoustic modes and thus is visco-elastic.

The boson-peak is seen best in the dynamic structure factor $S(q,\nu)$, which is shown in Fig. 2 for small values of q. From this figure we see that $\nu_{BP}(q)$, the location of the boson-peak, is q-dependent in that it moves from small frequencies for small values of q (dashed lines) to a maximum frequency for $q \approx 0.39$Å^{-1} (bold dotted line) and then back to small frequencies for large values of q (solid lines) (see also inset of Fig. 3). Also included is the location of the boson-peak as determined from neutron scattering experiments at 1673K which is around 1.5 THz [3]. We will comment more on this work below.

From the wave-vector dependence of ν_L and ν_T we obtain the dispersion relation which is presented in Fig. 3. We see that, as expected, for small wave-vectors ν_L depends linearly on q. Also included in the figure is a line with slope c_L=6370m/s, the experimental value of the longitudinal sound velocity of silica at around 1600K [3]. We see that the data points for ν_L for small q are very close to this line and thus we conclude that the sound velocity of this system is very close to the one of real silica, thus giving further support for the validity of the model potential.

For the transverse acoustic modes the agreement between the experiment and the simulation data is a bit inferior, but still good. We also note that for wave-vectors larger than 1.4Å^{-1}, a bit less than the location of the first sharp diffraction peak, ν_L and ν_T do not increase anymore. The reason for this is likely the fact that at this q value the system has a quasi-Brillouin zone [2].

Also included in the figure is ν_{BP}, the location of the boson-peak. We find that for large wave-vectors ν_{BP} is around 1.8 THz, a value that is a bit larger than the experimental value of 1.5 THz reported by Wischnewski et $al.$ at 1673K [3]. However, these authors also found that ν_{BP} increases with increasing temperature and a rough extrapolation of their data for ν_{BP} to T=2900K shows that a value of 1.8 THz is quite reasonable, thus giving further support for the validity of our model.

In the inset of Fig. 3 we show the dispersion curves at small values of q. Interestingly we observe that $\nu_{BP}(q)$ shows a maximum at around $q \approx 0.39\text{Å}^{-1}$. This maximum might be due to the fact that the mechanism leading to the boson-peak is particularly effective at this wave-vector or that there are two mechanisms giving rise to the boson-peak, one dominating at small wave-vectors and the second one dominating at larger wave-vectors and that in the vicinity of $q \approx 0.39\text{Å}^{-1}$ the sum of the contribution of the two mechanisms is largest.

Finally we mention that at small wave-vectors the curve for $\nu_{BP}(q)$ seems to join smoothly the one for ν_L. Within the accuracy of our data it is not clear, whether the boson-peak and the longitudinal acoustic mode become identical or whether the boson-peak ceases to exist for wave-vectors smaller than approximately 0.2Å^{-1} and thus we cannot use this feature to exclude one of the possible mechanisms proposed for the boson-peak.

To summarize we can say that our simulation allows to investigate the dynamics of supercooled silica in a wave-vector and frequency range which is not accessible to real experiments. We find that the dispersion relations for the longitudinal and transverse acoustic modes agree very well with the experimental values and that ν_{BP} shows a maximum at around 0.39Å^{-1}. This q corresponds to a length scale on the order of 15Å. Thus we have evidence that the mechanism leading to the boson-peak is very effective on the length scale of several tetrahedra.

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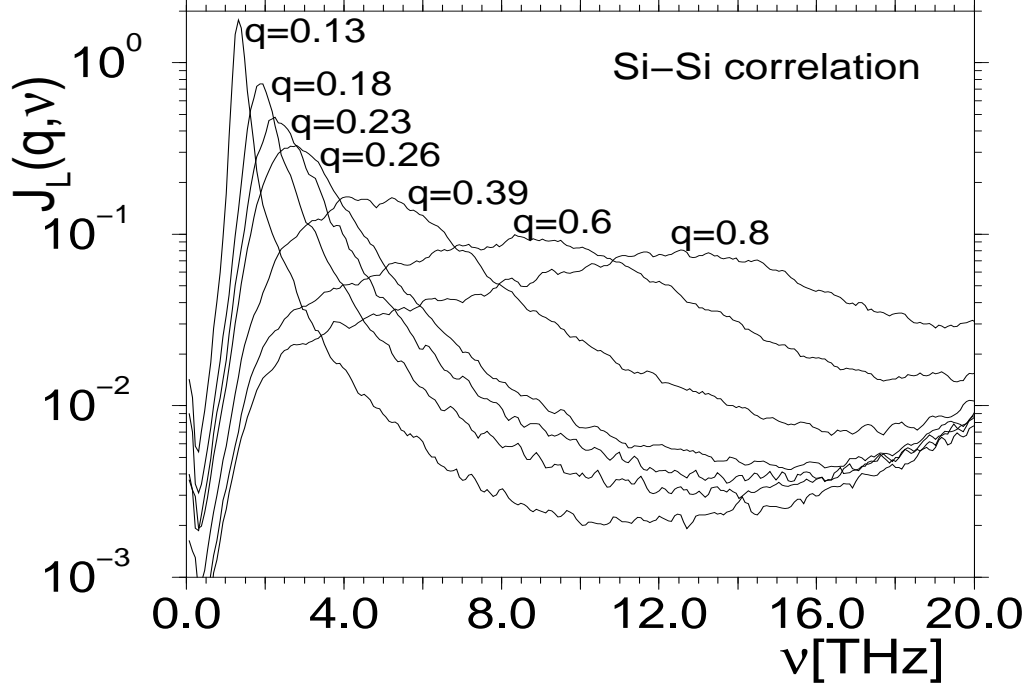[10] J. P. Boon and S. Yip *Molecular Hydrodynamics* (Dover, New York, 1980).

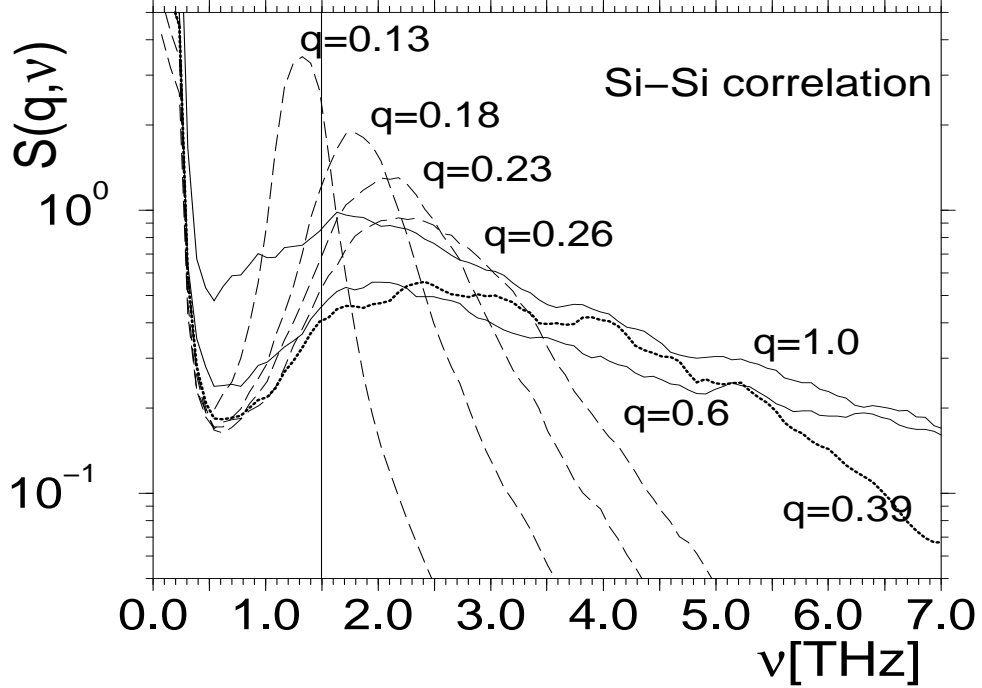FIG. 1. Frequency dependence of the longitudinal current-current correlation for different wave-vectors q.

FIG. 2. Frequency dependence of the dynamic structure factor for different wave-vectors q. The vertical line is the location of the boson-peak at 1673K as determined from the neutron scattering experiments [3].
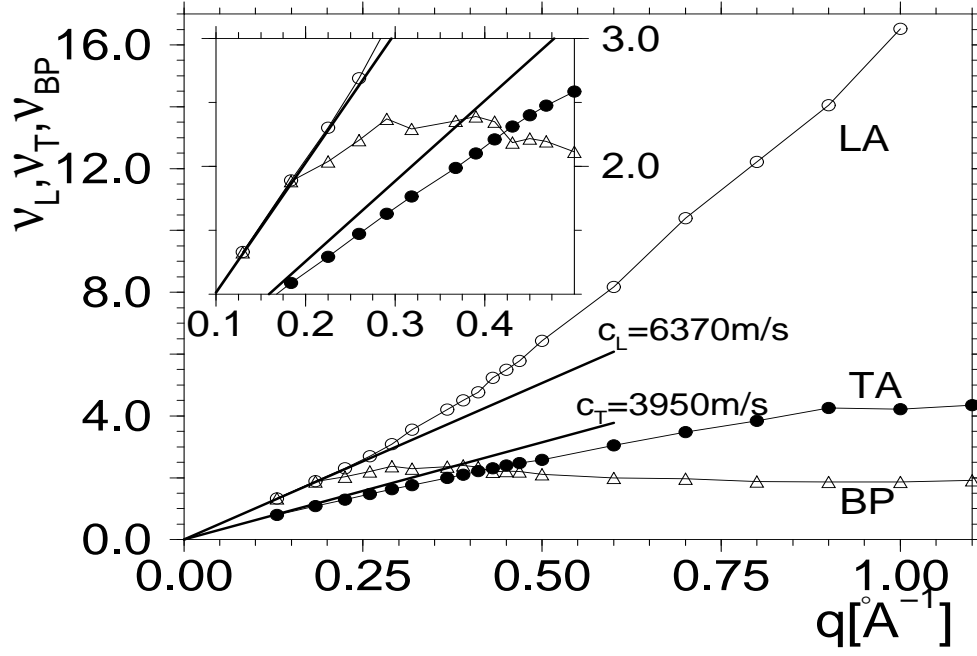
FIG. 3. Wave-vector dependence of ν_L (open circles), ν_T (filled circles) and ν_{BP} (open triangles). The bold solid lines are the dispersion relations for the longitudinal and transverse acoustic modes (Ref. [3]). Inset: enlargement of the curves at small q.